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PII: S0376-7388(15)30337-9
DOI: <http://dx.doi.org/10.1016/j.memsci.2015.11.038>
Reference: MEMSCI14131

To appear in: *Journal of Membrane Science*

Received date: 24 September 2015
Revised date: 22 November 2015
Accepted date: 23 November 2015

Cite this article as: Rahul Shevate, Madhavan Karunakaran, Mahendra Kuma and Klaus-Viktor Peinemann, Polyanionic pH-responsive polystyrene-b-poly(4 vinyl pyridine-N-oxide) isoporous membranes, *Journal of Membrane Science* <http://dx.doi.org/10.1016/j.memsci.2015.11.038>

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Polyanionic pH-responsive polystyrene-*b*-poly(4-vinylpyridine-N-oxide) isoporous membranes

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Abstract

Recently isoporous block copolymer (BCP) membranes obtained by non-solvent induced phase separation gained a lot of attention due to their highly ordered surface layer, high flux and superior separation properties. These polystyrene-*b*-poly-4-vinylpyridine (PS-*b*-P4VP) based membranes showed a strong flux dependence of pH; pores closed at low pH and opened at high pH. The pH-response could now be reversed by a simple post modification; pores are now opening at low pH and closing at high pH. The original membrane was transformed into a polyanionic pH responsive membrane in a one step chemical modification without affecting the isoporous surface morphology. A polystyrene-*b*-poly-4-vinylpyridine-N-oxide (PS-*b*-P4VPN-oxide) membrane is obtained by selective oxidation of the PS-*b*-P4VP membrane. The *in situ* generated peracid obtained by reacting acetic acid and hydrogen peroxide is employed for oxidation. Surprisingly not only the asymmetric membrane structure with the isoporous skin was retained, but also the mechanical and chemical membrane stability was improved significantly. The modified membranes are insoluble in solvents like DMF, NMP and DMSO. Two kinds of PS-*b*-P4VP based isoporous membranes are available now with reverse flux response to pH. This opens the door to new interesting charge based fractionations.

Keywords: Block copolymer membranes, PS-*b*-P4VPN-oxide, polyanionic isoporous membrane, self-assembly.

1. Introduction

Stimuli responsive membranes have recently received much attention because they have attractive potential applications in controlled drug delivery, biosensors, molecular recognition and molecular separation [1-4]. Stimuli-responsive membranes that can alter their properties and structures when subjected to specific external environmental conditions such as pH [5], temperature [6], ions [7], light [8], electric [9], and magnetic fields [10] are well known. Excellent examples of stimuli responsive biomembranes can be found in the human body, having versatile stimuli responsive biomembranes that regulate the body-functions by providing selective permeation of molecules or ions. The permeability and selectivity of such biomembranes have stimuli responsive characteristics and the bioinspired approaches provide excellent environmentally responsive materials that could bring a new dimension to materials science. To mimic such responsive membranes for molecular separations through membranes, nanoporous membranes with pore diameters tunable by external stimuli are necessary [11-13].

We have earlier reported the pH behaviour and selective protein diffusion through nanochannels of PS-*b*-P4VP membranes [14,15]. We showed the isoporous PS-*b*-P4VP membrane closes the nanochannel at acidic pH and opens at neutral and basic pH. We could now reverse this pH-responsiveness. By a simple chemical modification of the original PS-*b*-P4VP membrane we could tailor nanochannels, which open at acidic and close at basic pH. The membranes are produced via a one-step procedure by combining the self-assembly of an amphiphilic block copolymer (PS-*b*-P4VP) and non-solvent

induced phase separation, sometimes called self-assembly and non-solvent induced phase separation (SNIPS) method. The SNIPS process results in isoporous membranes composed of a uniformly nanoporous surface (separation layer) supported by a spongy macroporous sublayer. Membranes produced by the SNIPS method showed very high water flux and good solute rejections [16,17]. Numerous isoporous BCP membranes have been developed by the SNIPS method but few isoporous membranes have been reported to be stimuli responsive membranes [18-20].

Specifically, PS-*b*-P4VP and PS-*b*-P2VP isoporous block copolymer membranes are pH responsive; the pore walls of these membranes are lined with basic P4VP/P2VP blocks. The nitrogen atoms in the basic pyridine groups get quaternized under acidic condition. The PVP chains extend leading to pore closing of the nanoporous membranes. Under basic conditions, the pyridine groups neutralize and deswell to the original position leading to a reversible pore opening. These membranes are termed as polycationic membranes whereas membranes with opposite pH response are known as polyanionic membranes. To the best of our knowledge, no polyanionic isoporous block copolymer membranes have been reported by the SNIPS method. To obtain polyanionic membranes, the isoporous membranes should have acid functional groups ($-\text{COOH}$ and $-\text{SO}_3\text{H}$) on the pore walls either by pre-modification of the block copolymer (choosing a block copolymer having acid functional group before membrane formation) or by post modification of the block copolymer membrane (introducing acid functional groups after membrane formation). Isoporous block copolymer membranes having $-\text{COOH}$ or $-\text{SO}_3\text{H}$ groups by the SNIPS method have not yet developed. But efforts have been made for

surface/pore functionalization of isoporous membranes by post modification procedure to improve their properties and separation ability [15,21-23].

By considering the simple scalability, we chose the isoporous PS-*b*-P4VP membrane manufactured by the SNIPS method for post modification. However, a practical problem for the post modification process is that harsh reaction conditions and aggressive solvents can destroy the isopore geometry of the block copolymer membranes. In this study we introduced N-oxide groups by mild oxidation of the P4VP block to obtain polyanionic isoporous membranes. We hypothesize that an introduction of N-oxide charge moiety would swell/deswell the membrane pores with pH analogous to –COOH/–SO₃H groups. The oxidized PS-*b*-P4VP membrane maintained the isopore geometry after the modification and showed a reverse pH behavior to that of the original PS-*b*-P4VP isoporous membrane. The modified membrane was characterized and the pH responsive behavior of the membrane was studied.

2. Experimental Section

2.1 Materials

Polystyrene-*b*-poly-4-vinylpyridine block copolymer P9957-S4VP (PS-*b*-P4VP 139,000-*b*-40,000 g/mol; PDI = 1.1) and polyethylene glycol (PEG) of varied molecular weights (600, 3000, 10000, 35000 g /mol) were obtained from Polymer Source, Inc., Canada. N,N-dimethylformamide (DMF), 1,4-dioxane, ethanol (96%), nitric acid (HNO₃) and ammonium hydroxide (NH₄OH) were procured from Sigma Aldrich. Acetic acid (CH₃COOH; 99.8%) and hydrogen peroxide (H₂O₂; 35 wt.% solution) were purchased from Acros Organics. Tetrahydrofuran (THF) was received from Fischer Scientific. All

other chemicals were used without further purifications. Deionized (DI) water and water purified with a Milli-Q system (Millipore) was used in this study.

2.2 Membrane preparation

Membranes were prepared from a polymer solution containing 16.6 wt% PS-P4VP block copolymer in a mixture of 27.8 wt% DMF, 27.8 wt% 1,4-dioxane, and 27.8 wt% THF. The 16.6 wt% of BCP was added into the mixture of solvents (DMF, 1,4-dioxane and THF) and stirred for 24 h at room temperature (RT). The BCP solution was then cast on a glass plate using a casting knife with a gap height of 200 μm . The cast film was left at RT (22°C) for 10 s to partially evaporate solvents and then immersed into a coagulation bath of DI water until the membrane was peeled off from the glass plate. The fabricated membranes were thoroughly washed with DI water and ethanol to remove traces of solvents. The membranes were dried at RT for further modification and characterizations.

2.3 Membrane modification by selective oxidation under mild oxidizing condition

The flat sheet membrane was cut into 25 mm diameter pieces for further modification. The membranes were placed into a round bottom flask containing a mixture of CH_3COOH and H_2O_2 (1:1). The reaction was then performed at 50°C for 24 h under reflux condition to convert the P4VP groups into P4VPN-oxide as shown in Scheme 1. Afterwards, the membranes were taken out from the round bottom flask and thoroughly washed several times with DI water to remove traces of CH_3COOH or H_2O_2 . Finally, the cleaned membranes were kept in DI water before further characterization and use. It was noticed that the surface morphology of the membrane did not change after *in situ* oxidation at 50°C.

2.4 Membrane characterizations

The surface and cross-section morphology of the original and modified isoporous membranes were examined using a FEI Quanta 600, field emission scanning electron microscope (FESEM). Small pieces of membranes were dried under nitrogen atmosphere at RT. The dried pieces were fractured in liquid nitrogen to record cross-section images. The membrane samples were fixed on a specimen holder using a conductive carbon tape. To avoid charging problem, the membrane samples were sputter coated with gold for 60 s at 5 mA current in an argon atmosphere. The samples were then transferred to the SEM stage and the images were recorded on a FEI Quanta 600 at an accelerating voltage of 30 kV with varied magnifications. The membrane surface was characterized by AFM (Agilent, Model 5400) using a resonance frequency of 76-263 kHz in a tapping mode. The scan size for AFM images of the membranes was $2\ \mu\text{m} \times 2\ \mu\text{m}$; AFM images were used to obtain the surface roughness parameters. The water contact angle of membranes was measured via a sessile drop method using a contact angle goniometer (FM40, Kruss GmbH, Germany) equipped with video capture. 5 μL of DI water was carefully dropped on the membrane surface and the contact angle between water and membrane surface was measured using the goniometer. In addition, the image of water droplet on the membrane surface was captured with a camera (Stingray model, Allied Vision Technology, USA). For each membrane, the contact angle was measured at least five random locations of the membrane to minimize the experimental error and the average values were reported.

The outer surface zeta potential of the membranes was measured using the SurPass Electrokinetic Analyzer (Anton-Paar GmbH, Austria) in 10 mM NaCl solution at varied

pH in the range from 3 to 10. The pH of NaCl solution was adjusted automatically by addition of 10 mM HCl and NaOH solutions. Each data point represents an average of four measurements for each membrane. The outer surface zeta potential was estimated using the Helmholtz–Smoluchowski equation [24,25]. The viscoelastic properties of the membranes were evaluated using a dynamic mechanical analyzer (Q800TA Instruments, USA). The membranes were cut into a rectangular shape with 12 mm $\times$ 5.5 mm dimension and then clamped onto the film tension clamp of the instrument. The data for each membrane were recorded in a temperature range from 30 to 200°C at heating rate of 3°C/min under tension mode with amplitude of 15 μ m and 0.1 Hz frequency, respectively. The storage modulus (E'), loss modulus (E'') and loss factor ($\tan \delta = E''/E'$) values were calculated from the obtained data to evaluate viscoelastic behaviour of unmodified and modified membranes. Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra of membranes were recorded on a Thermo Scientific spectrometer (Nicolet iS10 model). The spectra were recorded over a wide range from 4000 to 1000 cm^{-1} for 16 scans with a resolution of $\pm 4 \text{ cm}^{-1}$.

2.5 Water flux and pH response

The pure water flux measurements were carried out in a stirred ultrafiltration cell (Amicon 8010, Millipore Co., USA). Acidic solutions were prepared using nitric acid of different concentration and basic solutions were made from ammonium hydroxide solution. The membrane was fixed in the ultrafiltration cell and the water flux measurement was conducted by filtering pH adjusted DI water at 1 bar feed pressure. The same procedure was applied for PEG rejection using a total PEG concentration of 0.4 wt% (0.1 wt% of each 600, 3000, 10000, 35000 g/mol). The samples of the feed solution,

retentate and permeate were collected after filtration at varied solution pH and analyzed using a gel permeation chromatography (GPC) system (Agilent Co.) equipped with dual column (Agilent PL Aquagel-OH 30 8 μ m, PL Aquagel-OH 40 8 μ m) setup and G1362A RID detector. The samples were filtered using a 5 μ m PTFE filter before injecting into a 1 ml/min carrier solution (ultrapure Milli-Q water, 18.2 M Ω).

3. Results and Discussion

3.1. Membrane preparation and morphology characterization

Highly ordered and self-assembled surface nanopores with uniform size are key factors for obtaining high flux and sharp molecular weight cut-off membranes. We used the reported method for fabrication of isoporous membranes from a amphiphilic diblock copolymer solution in a ternary mixture of solvents [16,18]. 16.6 wt% of PS-*b*-P4VP block copolymer was dissolved in a mixture of DMF, THF, and 1,4-dioxane (27.8 wt % of each). The membranes were formed after partial evaporation of THF, followed by immersion in DI water. An asymmetric membrane with highly ordered pores perpendicular to the surface with very high pore density and a non-ordered spongy sublayer was formed (**Fig. 1**). The average pore size of PS-*b*-P4VP and PS-*b*-P4VPN-oxide membranes were calculated from their surface SEM images using Image J software [26]. Minimum 250 pores were selected to obtain the average pore size of the membranes and the standard deviation (σ) values. The average pore size of the PS-*b*-P4VP membrane was 31.89 nm ($\sigma = \pm 10.98$ nm) and for the PS-*b*-P4VPN-oxide membrane the average pore size was 32.05 nm ($\sigma = \pm 11.18$ nm). These values confirm that no change in pore size of the membranes occurred after modification.

Fig. 1. Surface and cross-sectional SEM images a), b) PS-b-P4VP and c), d)

PS-b-P4VPN-oxide membranes.

It is

reported that solvent selection, concentration of solvents and block copolymer as well as evaporation time for solvent play an important role in formation of micelles and self-assembly [14,16,18]. Therefore, these parameters should be carefully controlled for fabrication of isoporous membranes by the SNIPS method. Finally, the block copolymer solution was precipitated in a non-solvent (DI water) and a highly ordered top layer membrane was formed. The conversion of the PS-b-P4VP membrane to PS-b-P4VPN-oxide was performed by selective *in situ* mild oxidation of P4VP block following an earlier reported method with a slight modification in the reaction temperature [27,28].

Scheme 1. Reaction route for modification of PS-*b*-P4VP membrane to PS-*b*-P4VPN-oxide membrane.

The reaction route for formation of PS-*b*-P4VPN-oxide using a mixture of acetic acid and H₂O₂ at 50°C is given in **Scheme 1**. At elevated temperature, peracetic acid is formed from a mixture of acetic acid and H₂O₂, which reacts with the pyridine units of the P4VP blocks of the pristine membrane and P4VPN-oxide blocks are obtained. Morphologies of unmodified (PS-*b*-P4VP) and modified (PS-*b*-P4VPN-oxide) membranes were assessed by recording their surface and cross-section SEM images (**Fig. 1 (a) and (b)**), respectively. The isoporous structure of modified membranes remains the same after the *in situ* mild oxidation at 50°C. In addition, the surface roughness parameters (R_a : average roughness, R_{ms} : root-mean square roughness, and R_{max} : maximum roughness) were obtained from AFM images of unmodified (PS-*b*-P4VP) and modified (PS-*b*-P4VPN-oxide) membranes (**Fig. 2**). The obtained values are reported in Table S1, Supporting Information. The R_a , R_{ms} and R_{max} values for PS-*b*-P4VP membranes were found to be 6.69 nm, 9.31 nm, 9.31 nm which are quite similar to the obtained values (6.83 nm, 9.34 nm and 9.34 nm) for PS-*b*-P4VPN-oxide membrane.

Fig. 2. Two dimensional a) and b); three dimensional c) and d) AFM images for PS-b-P4VP and PS-b-P4VPN-oxide membranes.

3.2. ATR-FTIR of membranes

The conversion of PS-b-P4VP membranes to PS-b-P4VPN-oxide membranes by the *in situ* oxidation reaction was confirmed by using FTIR. ATR-FTIR spectra for PS-b-P4VP and PS-b-P4VPN-oxide membranes are shown in **Fig. 3**. The broad absorption bands at 3400 cm^{-1} are related to the stretching vibration of -OH groups and residual water present in the membranes [28]. The intensity of the peak at 3400 cm^{-1} for the PS-b-P4VPN-oxide membrane is slightly increased because of associated water molecules. The absorption bands at 2913 and 3023 cm^{-1} are related to the aromatic stretching vibrations

of $-\text{CH}_2$ groups in the membranes. Two new peaks at 1178 cm^{-1} and 1230 cm^{-1} are

Fig. 3. a) ATR-FTIR spectra of PS-b-P4VP membrane. b) PS-b-P4VPN-oxide.

present in the FTIR spectrum of the PS-b-P4VPN-oxide membrane. These peaks are ascribed to oxygen bending vibration and N-O stretching vibration of N^+-O^- present in the PS-b-P4VPN-oxide membrane [28]. The shift in the absorption band from 820 cm^{-1} to 844 cm^{-1} is observed after *in situ* oxidation of PS-b-P4VP due to the contribution of planar oxygen bending vibration [29]. The obtained results confirm the successful conversion of PS-b-P4VP membranes to the PS-b-P4VPN-oxide form by mild *in situ* oxidation reaction at 50°C using a mixture of acetic acid and H_2O_2 . Based on the interpretation of the FTIR spectra and based on the dramatic change of water flux in response to pH (section 3.5) we assume a nearly total conversion of the pyridine groups to pyridine-N-oxide.

3.3. Membranes hydrophilicity and charge behavior

Hydrophilicity of the membranes was evaluated by determining their dynamic water

Fig. 4. a) Dynamic water contact angle of PS-b-PVP and PS-b-P4VPN-oxide membranes. b) the surface free energy of PS-b-PVP and PS-b-P4VPN-oxide membranes.

contact angle using a sessile drop method. The dynamic water contact angle, surface free energy and the snapshots of 5 μ l water droplets on the surface of PS-b-P4VP and PS-b-P4VPN-oxide membranes are depicted in **Fig. 4a and b**. The water contact angle value of the pristine membrane rapidly decreased with time and became zero after 1 min. This is due to the open pores of pristine membranes at neutral pH [14,18]. Therefore, water droplets rapidly penetrated into the membrane matrix. The water contact angle of modified PS-b-P4VPN-oxide membrane decreased slowly with time and became zero after 5 min. This is due to the resistance of closed pores of the membrane at pH = 7 for penetration of water droplets into the membrane matrix. The surface free energy of both membranes is found to be the same because of their similar water contact angle values

after 1 min time interval. These results clearly indicate that the hydrophilicity of modified membrane PS-b-P4VPN-oxide is similar. The surface charge of unmodified and modified membranes was studied by outer surface zeta potential measurements. The outer surface zeta potential (ζ) values for PS-b-P4VP and PS-b-P4VPN-oxide membranes in the pH range from 3 to 10 are shown in **Fig. 5**.

Fig. 5. The outer surface zeta potential values for PS-b-P4VP and PS-b-P4VPN-oxide membranes.

The positive outer surface zeta potential of the PS-b-P4VP membrane in acidic pH range from 3 to 5 is higher than that of the PS-b-P4VPN-oxide membrane because the protonated pyridine moiety of the pristine membrane allowed preferential adsorption of chloride ions [24,25]. The PS-b-P4VPN-oxide membrane did not allow adsorption of chloride ions due to electrostatic repulsion between the modified membrane and chloride ions. Furthermore, the negative outer surface zeta potential of PS-b-P4VPN-oxide membrane in basic pH range from 8 to 10 is lower than that of the PS-b-P4VP membrane

because the preferential adsorption of hydroxyl ions was hindered by the modified membrane.

3.4. Dynamic mechanical stability of membranes

Fig. 6 shows temperature dependent dynamic mechanical (storage modulus and $\tan \delta$) plots for PS-*b*-P4VP and PS-*b*-P4VPN-oxide membranes. Plots of the storage modulus as a function of temperature in **Fig. 6a** show that the dynamic storage modulus of modified membranes (PS-*b*-P4VPN-oxide) significantly increased to 20 MPa compared to pristine membranes (PS-*b*-P4VP), which is attributed to the enhancement in polymer inter chain bonding via charge-charge interactions [30].

Fig. 6. DMA analysis of PS-*b*-P4VP and PS-*b*-P4VPN-oxide membranes. a) temperature dependent storage modulus. b) $\tan \delta$ plots obtained from DMA.

The $\tan \delta$ plot in **Fig. 6b** also follows the same pattern as the storage modulus. The PS-*b*-P4VP membrane exhibited a well-defined relaxation peak at 120°C that is assigned to the glass transition temperature of the PS-*b*-P4VP diblock polymer. However, a slight shift in a relaxation peak from 120 to 140°C for PS-*b*-P4VPN-oxide membrane was obtained. These results clearly indicate that the segmental mobility of polymer chains is restricted

after *in situ* oxidation of PS-b-P4VP membrane at 50°C. The resulting modified membrane showed good mechanical stability for use in filtration application using the pressurized feed solutions.

3.5. Water flux and pH response characterization

The pH dependent water flux of the PS-b-P4VP membrane is presented in **Fig. 7a**. The water flux at lower pH (2 and 3) is low ($2.46 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) because the pyridine groups in the P4VP chains were protonated and became positively charged. Consequently, the

Fig. 7. a) pH dependent pure water flux of PS-b-P4VP membrane. b) pH dependent pure water flux of PS-b-P4VPN-oxide membrane at 1 bar feed pressure.

P4VP chains were stretched to minimize charge repulsion, leading to the reduction in effective pore sizes of the membrane [14,18,31]. High water fluxes of more than $1000 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ were obtained in basic pH range from 8 to 12. This was attributed to increased effective pore sizes of the membrane due to deprotonation of P4VP chains and their subsequently conversion into the coiled form at high pH [14,31]. Thus, pores of PS-b-P4VP membrane were opened and high water flux was achieved in basic pH. Similar observations were reported by Guo et al. applying dissipative particle dynamics

stimulation of pH sensitive micelles with histidine residues due to protonation of imidazole groups [32].

To achieve high water flux in acidic pH, the PS-b-P4VP membrane was converted into the PS-b-P4VPN–oxide form by mild *in situ* oxidation reaction at 50°C. The pH dependent water flux of the PS-b-P4VPN–oxide membrane is depicted in **Fig. 7b**. As expected, the water fluxes of the modified membrane in the basic pH region were found to be very low. This is because of a decrease in the effective pore size of the membrane due to chain stretching by negatively charged N–oxide.

The water flux of the PS-b-P4VPN–oxide membrane was high at low pH. The N^+-O^- groups in the P4VPN–oxide chains were converted into N^+-OH with change in pH from basic to acidic and consequently chain stretching was decreased. Thus, the pores of PS-b-P4VPN–oxide membranes were opened in acidic pH and the water flux was enhanced. A sharp change in water flux occurred in the pH range from 4 to 2. Hysteresis of more than 40% in water flux was observed at extreme pH values whereas the hysteresis in middle ranges was less than 20% when the pH increased or decreased from acid to basic or basic to acid region, respectively. Nunes et al. reported that the hysteresis in water flux is not attained from alkali to acid and acid to alkali regime when a PS-b-P4VP membrane is applied in ultrafiltration of DI water [14]. The observed hysteresis behaviour of the PS-b-P4VPN–oxide membrane is comparable to the hysteresis of a poly(styrene-alt-maleic acid) derived membrane reported by Xiang et al. [33]. The hysteresis of our modified membranes can be explained by the slow ionization of N^+-O^- groups in the membrane. More time is required to reach the equilibrium in comparison with the time for the pH dependent water flux measurements. Overall, the pH responsive behavior of the PS-b-

P4VPN–oxide membrane is completely opposite to the original PS-b-P4VP membrane.

Fig. 8 illustrates the swelling behavior of micelles in the PS-b-P4VPN–oxide membrane at low (pH = 2) and high pH (pH = 10). At low pH, the protonation of N^+-O^- groups in P4VPN–oxide block lowers the expansion of polymer chains and thus, the membrane pores are opened.

Fig. 8. Illustration of micellar swelling-deswelling and change in effective pore size of membrane with pH.

The membrane pores are closed at high pH because charge repulsion between chains of P4VPN–oxide moieties is dominant due to deprotonation of N^+-O^- groups. Thus, change in micelle dimensions has direct influence on water flux of PS-b-P4VPN–oxide membrane in acidic and basic pH. Ludwigs et al. also reported the pH dependent swelling and deswelling behavior of micelles derived from a triblock copolymer containing poly(methacrylic acid) block. Reversible swelling and deswelling behavior of micelles

were highly dependent on protonation of the poly(methacrylic acid) block [34].

A mixture solution of polyethylene glycol with nominal molecular weights 600, 3000, 10000, and 35000 g/mol was used to evaluate the membranes selectivity in acidic and basic region. When the PEG solution was filtered through PS-b-P4VP and PS-b-P4VPN–oxide membranes at low pH (2.2), the PS-b-P4VP membrane was able to retain 100% PEG of molecular weight 10,000 g/mol whereas PS-b-P4VPN–oxide membrane retained 20 % PEG of similar molecular weight (**Fig. S1**, Supporting Information and Table 1). Furthermore, at high pH (10.2) the PS-b-P4VP membrane had practically zero rejection for PEG of 10,000 whereas the PS-b-P4VPN–oxide membrane retained more than 90% PEG of 10,000 g/mol. The obtained results confirm pH switchable selectivity of the PS-b-P4VPN–oxide membrane towards PEG mixture solution because its pores open at low and close at high pH.

Table 1. Rejection (%) of various molecular weights PEG by PS-b-P4VP and PS-b-P4VPN–oxide membranes at low and high pH.

PEG (g/mol)	Rejection (%)			
	pH = 2.2		pH = 10.2	
	Membrane		Membrane	
	PS-b-P4VP	PS-b-P4VPN–oxide	PS-b-P4VP	PS-b-P4VPN–oxide
600	51.2	7.5	1.2	8.5
3000	94.2	16.4	1.6	50
10000	100	20	1.9	95.2
35000	100	27.1	5.2	100

3.6. Ethanol flux measurement

The original unmodified membranes showed a very low flux for 96% ethanol (around $1 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, **Fig. S2**, Supporting Information). This can be attributed to an excessive swelling of the P4VP block in ethanol leading to a drastic decrease in the effective pore size of PS-*b*-P4VPN membrane. In contrast the ethanol flux of the PS-*b*-P4VPN-oxide membrane remained high ($707 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$), showing that no or little swelling of the P4VPN-oxide chains occurred (**Fig. S3**, Supporting Information). Hence the PS-*b*-P4VPN-oxide membrane can be used in ethanol based separations. In addition, the PS-*b*-P4VPN-oxide membrane had better stability in various solvents in comparison with the pristine PS-*b*-P4VPN membrane (Table S2, Supporting Information). The modified membranes were found to be insoluble in all the studied solvents because the $^+\text{N}-\text{O}^-$ groups created a hindrance for the dissolution of P4VPN-oxide units in the solvents listed in Table S2. However, the binary or ternary mixture of solvents could be suitable to dissolve P4VPN-oxide units of the modified membranes.

4. Conclusion

In this study, we report a straight forward method to functionalize the isoporous PS-*b*-P4VP membrane via post modification reaction for obtaining a stimuli *pH* responsive isoporous membrane. Oxidation of the PS-*b*-P4VP membrane was carried out by *in situ* oxidation reaction using a mixture of acetic acid and H_2O_2 at 50°C . A PS-*b*-P4VPN-oxide isoporous membrane without distortion in morphology was obtained after post modification reaction at elevated temperature. ATR-FTIR technique confirmed the conversion of PS-*b*-P4VP membrane to PS-*b*-P4VPN-oxide. The conservation of the membrane's isoporous structure was also verified by AFM and SEM studies. The

hydrophilicity of the modified membrane did not change as confirmed by dynamic water contact angle measurements. The *pH* dependent water flux and PEG rejection studies in acidic and basic pH confirmed the polyanionic behavior of the PS-*b*-P4VPN-oxide membrane. The availability of a cationic PS-*b*-P4VP and an anionic PS-*b*-P4VPN-oxide with reverse pH response opens up an attractive way for pH-based separations.

Acknowledgement

The authors gratefully acknowledge financial support from King Abdullah University of Science and Technology (KAUST) with special thanks for funding from the KAUST CRG2 project “Charge-Mosaic and Block Copolymer Membranes”.

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Figure Captions

Fig. 1. Surface and cross-sectional SEM images of (a), (b) PS-*b*-P4VP and (c), (d) PS-*b*-P4VPN–oxide membranes.

Fig. 2. Two dimensional a) and b); three dimensional c) and d) AFM images for PS-*b*-P4VP and PS-*b*-P4VPN–oxide membranes.

Fig. 3. a) ATR-FTIR spectra of PS-*b*-P4VP membrane. b) PS-*b*-P4VPN–oxide membrane.

Fig. 4. a) Dynamic water contact angle of PS-*b*-PVP and PS-*b*-P4VPN–oxide membranes. b) The surface free energy of PS-*b*-PVP and PS-*b*-P4VPN–oxide membranes.

Fig. 5. The outer surface zeta potential values for PS-*b*-P4VP and PS-*b*-P4VPN–oxide membranes.

Fig. 6. DMA analysis of PS-*b*-P4VP and PS-*b*-P4VPN-oxide membranes. a) temperature dependent storage modulus. b) $\tan \delta$ plots obtained from DMA.

Fig. 7. a) pH dependent pure water flux of PS-*b*-P4VP membrane. b) pH dependent pure water flux of PS-*b*-P4VPN–oxide membrane at 1 bar feed pressure.

Fig. 8. Illustration of micellar swelling-deswelling and change in effective pore size of membrane with pH.

Graphical Abstract

Highlights

- Polyanionic pH-responsive isoporous block copolymer membranes were prepared.
- The membranes were synthesized by a chemical post-modification of PS-*b*-P4VP membranes.
- The membrane pores are opening at low pH and closing at high pH.
- The post-modification improved the mechanical and chemical stability of the membranes.